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INTERPRETING IR DIFFERENCE SPECTRA.

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normalized interfacial Fourier transform infrared spectroscopy, SNIFTIRS, electrochemically modulated infrared reflectance spectroscopy, EMIRS, or similar infrared spectroelectrochemical techniques, as well as some microsample analyses, studies of biochemical processes, and infrared astronomical observations, to name just a few examples. A mathematical evaluation of the problem is offered to demonstrate what information may realistically be gained from the characteristics of difference spectra. It is shown that in the worst case, where frequency, intensity, and peak width are all changing due to some perturbation of the sample (e.g., from temperature, or surface potential changes between background and sample spectra, etc.), even a qualitative interpretation may not be possible. In many practical cases, however, we show that at least a qualitative interpretation of the data can be obtained from difference spectra. Spectroelectrochemical applications for the calculations shown here are presented as examples, although these results impact a wider range of applications.

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INTERPRETING IR DIFFERENCE SPECTRA

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ABSTRACT: From the evaluation of sample difference spectra based on Gaussian "model" peaks with known peak characteristics, it is shown that interpretation of some parameters from difference spectra, resulting from the ratioing or subtraction of a poor background spectra, may be inaccurate or misleading. Difference spectra of this type are commonly observed using techniques such as subtractively normalized interfacial Fourier transform infrared spectroscopy, SNIFTIRS, electrochemically modulated infrared reflectance spectroscopy, EMIRS, or similar infrared spectroelectrochemical techniques, as well as some microsample analyses, studies of biochemical processes, and infrared astronomical observations, to name just a few examples. A mathematical evaluation of the problem is offered to demonstrate what information may realistically be gained from the characteristics of difference spectra. It is shown that in the worst case, where frequency, intensity, and peak width are all changing due to some perturbation of the sample (e.g., from temperature, or surface potential changes between background and sample spectra, etc.), even a qualitative interpretation may not be possible. In many practical cases, however, we show that at least a qualitative interpretation of the data can be obtained from difference spectra. Spectroelectrochemical applications for the calculations shown here are presented as examples, although these results impact a wider range of applications.

INTRODUCTION

Subtraction of a reference spectrum from a sample spectrum generates a difference spectrum with grating infrared techniques. Similarly, ratioing a background spectrum to a sample spectrum to produce what is also commonly known as a difference spectrum is a widely used method for obtaining data using Fourier Transform Infrared Spectroscopy. In general, these difference spectra techniques are used to eliminate interference from detector response characteristics in combination with optical characteristics of mirrors, sample handling materials (e.g., infrared transparent salts) and other non-sample infrared absorbers in the beam path (e.g., water vapor, CO_2). The best sample data will be obtained using a background spectrum where the sample is removed without disturbing anything in the beam path.

In most applications, however, background selection is difficult at best. Spectroscopy of surface adsorbates provides a challenge, since it involves a non-trivial effort to collect a background from a "clean" surface and then coat that surface without irreversibly moving the sample in a way that changes the optical path and renders the background useless. A prime example of difficulty in obtaining acceptable background spectra for surface applications occurs in spectroelectrochemistry. Other areas where background collection may be difficult (and weak sample spectra may be anticipated) include infrared microsample analysis, infrared studies of complex biochemical processes, and infrared astronomic measurements. The signal of interest in each of these applications is generally weak, and either background selection is difficult, or separation of the weak sample signal from strong background interference requires the use of difference spectra. For illustrative purposes, spectroelectrochemical systems will most frequently be used as examples here.

Two of the more commonly used techniques in infrared spectroelectrochemistry are known as SNIFTIRS, or subtractively normalized interfacial Fourier transform infrared spectroscopy, and EMIRS, or electrochemically modulated infrared reflectance spectroscopy. Both techniques employ a thin layer cell, where a 1-3 μm layer of electrolyte is sandwiched between an infrared transparent window and an electrode surface. Difference spectra are collected by ratioing spectra collected while the electrode is held at one reference potential with spectra collected at a series of sample potentials. If the reference potential can be selected such that no adsorbate is on the surface, and such that there is no overlap between absorbing solution species and the surface species of interest, then the resulting spectra are fairly easy to interpret, as peak position and intensities as a function of potential can be determined. However, due to a limitation in accessible potentials, it is often experimentally impossible to reach a potential at which there is no adsorbate on the surface. Also, overlap between spectra of species in solution and spectra of surface species is common. In these instances, it is much more difficult to extract meaningful data from the resulting difference spectra. EMIRS provides similar data, although the method is slightly different. For EMIRS, radiation is specularly reflected from a polished electrode surface while the electrode potential is modulated with a square waveform. The signal observed in an EMIRS experiment is proportional to the difference in the intensity of radiation received by the detector while the electrode is at one of the two fixed potentials defined by the square wave modulation. This intensity difference is represented in spectra as a reflectivity difference, ΔR, which may have a number of sources (instrument or sampling characteristics) besides changes in the amount of adsorbed species near the electrode. By ratioing ΔR with a reference, electrochemists attempt to remove detector contributions to spectra, and other instrumental characteristics. The EMIRS spectra, like the SNIFTIRS spectra, correspond to difference spectra between species present at the two selected electrode potentials. Examples of spectroelectrochemical systems studied, many using difference spectra, may be found in two recent reviews of the subject.[1,2] The purpose of this paper is to discuss the pitfalls of some quantitative interpretations of difference spectra specifically in terms of the problems occurring using SNIFTIRS, EMIRS, or similar techniques, and to provide an idea of what quantities or trends may realistically be extracted from these data.

There are prior examples in the area of spectroelectrochemistry where the problems incurred by using difference spectra have been recognized. Two papers[3,4] have discussed the origin of EMIRS difference spectra, and Bewick et al.[3] include a discussion of the possible problems in determining exact frequency and intensity information from difference spectra, as well as a discussion of other pitfalls of the EMIRS technique.

When it is possible to obtain high enough signal/noise so that IR peaks from the sample of interest are visible in untreated spectra, mathematical expressions which were derived to describe infrared and Raman difference spectra can be applied to determine quantitative information from the data. In these cases, the papers by Laane[5] and Laane and Kiefer[6] on Raman difference spectroscopy, and infrared and Raman difference spectroscopy[7] may be extremely useful. Similarly, work by Brown et al.[8] may help in the extraction of useful information from difference spectra, especially in the recognition of spectral artifacts. While this work has some applications to the infrared difference spectroscopy, much of it cannot be applied to SNIFTIRS, EMIRS and other data arising from weakly absorbing samples since the mathematical formulae depend on the experimentalists knowing the intensity, peak width, and frequency data of their original spectra. In the case of SNIFTIRS and EMIRS, electrochemists probe adsorbates in the submonolayer to monolayer regime with p-polarized light which enhances the contribution from the surface over contribution from solution species. For typical solution concentrations of 10 mM used in these thin layer cell experiments, the amount of adsorbate molecules in the beam path is equivalent to ca. 1 monolayer. The total spectral feature from such a small number of molecules is usually too weak to be visible in the raw spectra. Therefore, the application of these existing calculations to spectroelectrochemistry or techniques with similar limitations is not universal, since parameters necessary to solving the equations for difference spectra are not always available. In fact, many of the applications that depend on difference spectra do so because the peaks of interest in the raw spectra do not have sufficient signal to be identifiable without background subtraction.

DISCUSSION

Experimentally, it is useful to understand how the individual peak characteristics provide information on chemical or physical properties of a system studied by infrared difference spectroscopy. Again, spectroelectrochemical systems may be used as an example, because there are a number of spectral characteristics which are used to understand the adsorption behavior at the electrode surface. To show that an adsorbate is at the surface, one of the characteristics that electrochemists look for is a shift in adsorbate peak position with potential. Since the electric field drops off rapidly with distance from the electrode surface, only those molecules very near the surface should be affected by potential changes. Along with peak position, differences in infrared peak intensities, peak widths, or peak number may also be observed. The formation or loss of spectral peaks may suggest that a substantial change has occurred at the surface, commonly either a restructuring of the adsorbate on the metal, or a chemical reaction at the surface. Changes in peak width are also observed and have been interpreted to reflect a change in orientation or strength of bonding with the surface or a change in lateral interactions with other adsorbate molecules. Variations in peak intensity are usually taken to indicate a change in the adsorbate surface coverage or the number of molecules in a given orientation. For any of these parameters, the ability to obtain some quantitative description of the change that has occurred is of great importance in determining what interactions are taking place between the electrode and an adsorbate. Similar types of information may be of interest to researchers outside electrochemistry, but the basic importance of peak characteristics is fairly universal for many applications of infrared spectroscopy.

A raw spectrum contains a great deal of information that is not easily separable into its individual components. The detector response, absorption by optics, sample handling devices, and the atmosphere in the sample chamber will all contribute to give the total absorption spectrum. Optical considerations for some of the spectroelectrochemical cells have been recently described in detail[9] and were shown to dramatically influence the appearance of the spectrum. Looking at the raw sample spectrum, particularly in the case of weakly absorbing samples or small number of absorbers, will frequently not provide much information until a difference spectrum is obtained. In order to compare the sample and reference raw spectra with the difference spectrum obtained by subtraction, with grating instruments, or by ratioing, with FTIR instruments, we will look at the relationship between the peaks in simple model raw spectra with the spectrum that can be obtained by subtracting model reference from model sample spectra. The term "ratioing" which describes the mathematical operation used to remove background information in FTIR spectra, may at first seem not to lend itself to this subtraction modelling. However, the actual operation of ratioing may be viewed as shown in equation (1): If σ represents a small change in the absorbance, then the ratio of FTIR spectra may be written:

$$\frac{(1-\sigma_{E_r})}{(1-\sigma_E)} \approx (1-\sigma_{E_r})(1+\sigma_E) \approx 1+\sigma_E-\sigma_{E_r} \qquad (1)$$

for σ_{E_r} and $\sigma_E << 1$, and assuming that σ^2 is negligible compared to σ, where E represents a sample potential, and E_r represents a reference potential (Unity, seen in the last form of the equation, is the 100% line). Electrode potential is used here as an example perturbation from electrochemistry, but other perturbations may be substituted. The difference in σ values provides the spectral information. Therefore, to simplify the discussion we will ignore the 100% line and limit our analysis to the difference $\sigma_E - \sigma_{E_r}$. The models will apply to difference spectra attained either through direct subtraction or ratioing of the sample and reference spectra.

With this understanding, a very good reference for some hypothetical system may be approximated by a line at zero intensity. If we subtract our zero line from any sample peak, approximating a difference spectrum, we will simply get the original sample peak back. In this case, as in the case where the reference spectrum contains no surface adsorbate information, all of the features in the sample spectrum are preserved. Any measurements of peak position, intensity, width, or number of peaks will then provide true quantitative information of surface interactions. Now, suppose that we subtract the sample from our zero reference. The resulting spectrum is the same as the real sample, only negative in intensity. Peak position and width are preserved. In this case it is still possible to determine what the actual sample spectrum contains.

By using a Gaussian or Lorentzian model for a set of peaks, we can describe a series of single peak spectra. These model peaks can be generated with the three main characteristics which have been discussed so far; namely, a defined peak position, width, and amplitude. If we select one of the peaks as a background by subtracting it from the others, we can model what would occur in difference spectra when a background containing some contribution from the adsorbate is used. In an experiment requiring background subtraction before IR peaks can be observed, we cannot know the actual sample component of a raw spectrum unless we can determine it from the difference data. Using our Gaussian and Lorentzian models, we will compare a set of well-defined, or "real," sample spectra with the "observed" difference spectra. It should then be possible to determine how the two sets of spectra are related.

It is possible to generate a great variety of both single and bipolar peak shapes by varying the parameters of sample and reference spectra independently. This variety makes discussion of all the appearances of difference spectra prohibitive. For this reason, we have chosen a number of examples to demonstrate the behavior of single and bipolar peaks in difference spectra when parameters are modified in a way that is likely to be found in some experiment. Starting from single peak sample and reference spectra, it is possible to generate single peaks, bipolar bands, and even three peak difference spectra. We will begin by looking at single peaks in difference spectra, and following this will be some examples of the characteristics of bipolar difference spectra. A more mathematical analysis of both types of spectra will be included at the end of each set of examples to demonstrate that some rules may be applied to the interpretation of the characteristics of common difference spectra.

The cases to be studied are chosen as follows: Cases 1 through 5 are representatives of single peaks in difference spectra which vary in peak shift direction (Cases 1 and 2), magnitude of the peak shift (Case 3), peak intensity with peak shift (Case 4), and peak intensity and peak width with a shift in frequency (Case 5). Cases 6 through 8 are representatives of bipolar difference spectra, where the reference peak intensity and peak position is varied (Cases 6 and 7), and only the peak position is varied (Case 8).

SINGLE PEAKS IN DIFFERENCE SPECTRA

As a first case for single peaks generated in difference spectra, let us consider a shift in peak position. Peak shifts are often found between difference spectra collected by varying the electrode surface potential in spectroelectrochemical experiments. By changing the Gaussian peak frequency $+10 cm^{-1}$ across a range of six model peaks, while the intensity also increases by +10 arbitrary intensity units over the same range, it is possible to generate the sample spectra found in Fig. II. "A" in Fig. I will then be used as a reference which will be subtracted from the simulated "real" peaks B, C, D, and E. F represents a zero line which cannot be obtained in some actual experiments, but can be used to provide a "real" limit for our calculations. The difference spectra resulting from the subtraction of "A" from "B" through "F" are shown in Fig. III. The parameters used in the Gaussian peaks are summarized in Table I. Case I. The "observed" peaks, designated "B-A" etc. in Fig. III look very different from the "real" peaks shown in Fig. II. The more intense the "real" peak, the weaker the "observed" peak, although the amplitude has a negative sign. The "real" peaks vary in position from 102-110 cm^{-1}, while the "observed" peaks vary from 110-117.1 cm^{-1}. The peak widths were not varied. This first test, then, already shows that the exact peak positions are not preserved in difference spectra. The trend for increasing peak frequency with potential is conserved, along with the increase in peak intensity with potential. A plot of "observed" vs. "real" wavenumber position for this data can be seen in Fig. 2. The actual peak shift observed is slightly smaller than the "real" value, $+7.1 cm^{-1}$, instead of $8 cm^{-1}$ dictated by the original peak parameters.

The peak characteristics which change as the result of some increasing perturbation have a number of interpretations, and the relationship between the observed changes and spectral interpretations are often demonstrated in spectroelectrochemical research. For example, it is not uncommon for adsorbate coverage to increase at an electrode surface as the electrode potential is increased. This increase in surface coverage results in an increase in the intensity of infrared peaks characteristic of the adsorbate. Also, as adsorbate molecules are forced to interact with the surface in the electric field near the electrode, the molecules may react or be fixed on the surface in such a geometry that a potential dependent shift in peak frequency may also be observed. This peak shift with potential is often called a tuning rate. Tuning rates are often reported as an important indicator of the type of electrode surface interaction occurring. Therefore, this first example is of direct interest to spectroelectrochemists, as the results here show that selection of a background potential where some adsorbate features are included in the background spectrum will lead to measurement of an incorrect tuning rate from the difference spectra. Selection of such a background is common, for example, in experiments within the double-layer potential region (the voltage region where no Faradaic processes occur). Some adsorbate is likely to be present on the surface at all potentials within this region, if adsorption occurs in this region at all.

Let us return to a more general approach and consider a second example, again considering single peak difference spectra. If the direction of the peak shift is reversed, so that a "real" peak position shift of $-10\ cm^{-1}$ is used, and the intensity still increases by 10 arbitrary intensity units, the curves in Fig. 3 are generated. The parameters for this case are found in Table 1, Case 2. From the graph of these data in Fig. 2, it is apparent that the "observed" peak shift is reversed in sign, so that it is consistent with the "real" data. However, in this case again the value of the peak shift is smaller than the "real" peak shift, $-7.1\ cm^{-1}$ instead of $-8\ cm^{-1}$.

By increasing the tuning rate in the same "real" tuning direction as in Case 2, we develop the peaks used in Case 3. The parameters for this example are in Table 1, Case 3. The only difference between Cases 2 and 3 is that the shift in peak frequency is now $-20\ cm^{-1}$. Once again the direction of the "observed" shift is correct, but the "observed" shift is smaller, ca. $-11.1\ cm^{-1}$, instead of $-16\ cm^{-1}$. It appears that the larger the "real" peak shift, the worse the match is between the "real" and "observed" data. The "observed" rate errs by being too small, at least for the case where the peak shift is the only parameter altered. A plot of "observed" vs. "real" wavenumber position for Case 3 is also included in Fig. 2.

For Case 4, the parameters used in the first case were altered by changing the intensity variation, as shown in Table 1, Case 4. The "real" peak shift is $+8\ cm^{-1}$, and the observed peak shift was found to be $+5.8\ cm^{-1}$. In Fig. 2 the plot of the "observed" vs. "real" wavenumber position indicates that the "observed" data are not linearly related to the "real" data if the intensity is varied by a large and nonlinear amount.

Case 5 is one of the worst experimental cases; where the intensity variation is not linear with potential, peak positions change, and there is a change in the peak width. The parameters used in this case are in Table 1, Case 5. In the curve in Fig. 2 for these data, the nonlinearity in the relation between "observed" and "real" wavenumber positions becomes even more exaggerated than in Case 4. The "observed" peak shift for this example is $+14.2\ cm^{-1}$, much larger than the "real" shift of $+8\ cm^{-1}$. Increasing the peak width with increasing intensity then appears to increase the "observed" peak shift for this example. The direction of the shift is not conserved over the entire range of peaks considered here, so depending on experimental parameters (such as the varying of potential, time, temperature, or other perturbation to obtain more than one difference spectrum), and the range within the experimental parameter chosen, completely different results could be reported based on difference spectra measurements.

To take a look at the "observed" intensities vs. the "real" intensities for Cases 1 through 5, the relationships between these values were plotted in Figs. 4A to E, respectively. From this figure it appears that the relationships are more linear than those of the frequencies for the same sets of parameters. In Cases 1 and 2, where the direction of the peak shift is changed, but not the intensity differences, the "observed" intensity variation is 7.9 intensity units instead of 8. In Case 3, where the peak shift was doubled from Case 2, the "observed" intensity variation was 7.6 intensity units instead of 8. In Cases 4 and 5, where the intensity was varied in a slightly nonlinear fashion, the observed rates were 18.8 and 18.5 intensity units, instead of 19, respectively. Therefore the change in peak widths found in Case 5 had only a slight affect on the peak intensity. The very small differences between "real" and "observed" intensities seen in these results are extremely encouraging, and suggest that interpretations based on peak intensities in real systems similar to those in Cases 1 through 5 are reliable, at least over the examples recorded here.

Mathematically, it is possible to work out at least the peak shift relationship observed in these model data. Assume, by way of example, that we are interested in studying the effects of changing the electrode potential on species found near the electrode surface, and that a reference spectrum is collected at some potential, E_r, and it will be ratioed against a spectrum collected at some sample potential, E. In order to show the relationship between the "real" and "observed" data, if we assume that the peak width is constant, we manipulate two Gaussian spectra as follows:

$$I(E, \nu) = a e^{-\frac{(\nu - \nu_E)^2}{2\sigma^2}} \tag{2}$$

$$I(E_r, \nu) = b e^{-\frac{(\nu - \nu_{E_r})^2}{2\sigma^2}} \quad . \tag{3}$$

where ν_{E_r} denotes the frequency at the reference potential, σ is the peak width, and I is the intensity at the designated frequency.

Let $\Delta I = I(E,\nu) - I(E_r,\nu)$. If we set $\frac{\partial \Delta I}{\partial \nu} = 0$, we can obtain the "observed" peak positions, ν_p.

$$0 = I(E, \nu_p)\left[-2\frac{(\nu_p - \nu_E)}{2\sigma^2} \right] - I(E_r, \nu_p)\left[-2\frac{(\nu_p - \nu_{E_r})}{2\sigma^2} \right] \tag{4}$$

$$\nu_p[I(E_r, \nu_p) - I(E, \nu_p)] = \nu_{E_r}[I(E_r, \nu_p) - \left(\frac{\nu_E}{\nu_{E_r}}\right) I(E, \nu_p)] \tag{5}$$

From equation (5), it is possible to observe a number of characteristics relating the "real" and "observed" spectra, including the quantity that spectroelectrochemists call the "tuning rate," or T, that actually describes the change in peak position with potential, or $\frac{\partial \nu}{\partial E}$. For other applications, the "T" used here represents the change in peak position caused by some perturbation (e.g., time, temperature, distance, etc.).

$$\text{If } T > 0,\ E_r > E,\ \text{then } \nu_p > \nu_{E_r}(\text{ or } \nu_E) \text{ and } T_{obs} > 0 \tag{6}$$

which is observed in Case 2, as shown in Figure 3.

$$\text{If } T < 0,\ E_r > E,\ \text{then } \nu_p < \nu_{E_r}(\text{ or } \nu_E) \text{ and } T_{obs} < 0 \tag{7}$$

which is observed in Case 1, as shown in Figure 1.

$$\text{if } T = 0,\ E_r > E,\ \text{ then } \nu_p = \nu_{E_r}(\text{ or } \nu_E) \text{ and } T_{obs} = 0 \qquad (8)$$

For the real experimental data where the peak shapes are more Lorentzian, a similar calculation may be performed. Let the sample and reference potentials be represented by:

$$I(E, \nu) = \frac{a}{[(\nu - \nu_E)^2 + (\sigma/2)^2]} \qquad (9)$$

$$I(E_r, \nu) = \frac{b}{[(\nu - \nu_{E_r})^2 + (\sigma/2)^2]} \ . \qquad (10)$$

Then,

$$\Delta I = \frac{a}{[(\nu - \nu_E)^2 + (\sigma/2)^2]} - \frac{b}{[(\nu - \nu_{E_r})^2 + (\sigma/2)^2]} \ . \qquad (11)$$

Again, if $\frac{\partial \Delta I}{\partial \nu} = 0$ then we can obtain the "observed" frequency positions, ν_p.

$$0 = \frac{2a(\nu_p - \nu_E)}{[(\nu_p - \nu_E)^2 + (\sigma/2)^2]^2} - \frac{2b(\nu_p - \nu_{Er})}{[(\nu_p - \nu_{E_r})^2 + (\sigma/2)^2]^2} \qquad (12)$$

$$\frac{[(I(E, \nu_p))^2]}{a}(\nu_p - \nu_E) = \frac{[(I(E_r, \nu_p))^2]}{b}(\nu_p - \nu_{E_r}) \qquad (13)$$

$$\frac{\nu_p[(I(E_r, \nu_p))]^2}{b} - \frac{[I(E, \nu_p)^2]}{a} = \frac{\nu_{E_r}[(I(E_r, \nu_p))]^2}{b} - \left(\frac{\nu_E}{\nu_{E_r}}\right)\frac{[I(E, \nu_p)]^2}{a} \quad (14)$$

which yields the same relationship between ν_p, ν_E, ν_{E_r}, and the peak shift as observed in the Gaussian calculation.

It is possible to see from equations (5) and (14) that the sign of the peak shift will be conserved in difference spectra in which there are no changes in the peak width. Case 5, where the peak width does vary, is an example where the direction of the frequency shift is not conserved in the difference spectra. This is shown more clearly in Fig. 2c, where the slope of the line in the plot of "observed" frequency vs. "real" frequency does not always have the same sign. In IR spectroelectrochemistry (again as an example), one can expect to report the correct direction of the peak shift, or tuning rate, in cases where peak widths do not vary. Modelling of experimentally determined difference spectra by sums of Gaussian (or Lorentzian) peaks with positive or negative amplitudes may serve to help determine whether peak widths have changed as a function of potential differences. While peaks in difference spectra do not often look Gaussian or Lorentzian, sums of Gaussian or Lorentzian peaks frequently have the appearance of difference spectra collected in experiments. This sort of modelling has already been applied to some infrared spectroelectrochemical difference spectra,[10,11] although quantitative determination of tuning rates from this data was still not realistic. The modelling that was done, however, showed that the peaks observed could be reasonably fitted without varying the peak widths of the sample and reference spectra with potential. Therefore the sign of any shifts observed should be correct.

BIPOLAR PEAKS IN DIFFERENCE SPECTRA

Possibly more familiar forms of difference spectra to spectroelectrochemists and others are those that have some "zero crossing" point, where the spectrum has both positive and negative peaks. To evaluate data of this sort, it is frequently assumed that the position of the positive feature represents the spectroscopy of the surface at one potential, time, temperature, or other parameter, while the negative peak is due to absorption by species at a second potential, time, temperature, etc., and a bipolar band results. These peaks are also evaluated in terms of their frequency and intensity, and occasionally their peak widths. We have generated some of these spectra in Cases 6 through 8 (see Table 1 for peak parameters.) In Case 6, a Gaussian peak with a lower intensity, but higher peak frequency, was used as a reference. Case 7 may be one of the more common cases, where the relative peak widths are narrow enough and the peak frequencies are far enough apart, that the resulting difference spectra have some bipolar characteristics. Case 8 is the most ideal of these three cases, where intensity and peak width are held constant, and only the frequency is varied. Figures 5 through 7 show the appearance of the data from Cases 6 through 8, respectively.

Assuming that both the positive and negative peaks arise from the same molecular vibration, then the determination of the peak shift from the difference spectra is of interest. In Fig. 8, plots of "observed" vs. "real" frequency for the positive and negative bands are shown. For comparison, a line showing the ideal or "real" peak shift is included. It is obvious from both Figs. 8a and b that the peak shifts determined by measuring peak positions from the positive and negative peaks in the difference spectra are not the same as the "real" peak shifts. The actual peak positions seem to fall in-between the peaks observed in the difference spectra. Figure 9 shows that the "observed" peak intensities are also non-linear when the "real" peak intensities are linear, as seen in Table 1, Cases 6 and 7.

Case 8 is an interesting example where, while the peak positions are not accurate measures of the peak shift, the peak shift is related to the position of the zero crossing point. In this example, with only the frequency changing with potential (or other perturbation), the following calculation prov... the relationship between "real" and "observed" peak shifts:

For Gaussian peak shapes: $I(E, \nu) = I_0 e^{-\frac{(\nu - \nu_E)^2}{2\sigma^2}}$

$$I(E_r, \nu) = I_0 e^{-\frac{(\nu - \nu_{E_r})^2}{2\sigma^2}} , \tag{15}$$

where ν_E is the frequency at some sample potential, and ν_{E_r} is the peak frequency at some reference potential. Considering the zero crossing point equation in the difference spectrum:

$$\Delta I = I_0 e^{-\frac{(\nu - \nu_E)^2}{2\sigma^2}} - I_0 e^{-\frac{(\nu - \nu_{E_r})^2}{2\sigma^2}} \tag{16}$$

since $\Delta I = 0$ at the zero crossing point. If the intensities and peak width do not change with potential, and ν_z is the frequency at the zero crossing point, then:

$$(\nu_z - \nu_E)^2 = (\nu_z - \nu_{E_r})^2 , \tag{17}$$

so

$$\nu_z - \nu_E = \pm(\nu_z - \nu_{E_r}) . \tag{18}$$

For the $+(\nu_z - \nu_{E_r})$ case. $\nu_E = \nu_{E_r}$.

For the $-(\nu_z - \nu_{E_r})$ case,

$$2\nu_z = \nu_E - \nu_{E_r} \tag{19}$$

$$\nu_z = 1/2(\nu_E - \nu_{E_r}) \tag{20}$$

$$\frac{\partial \nu_z}{\partial E} = \frac{1}{2}\frac{\partial \nu_E}{\partial E} . \tag{21}$$

Similarly, for the case where the peak shape is more Lorentzian, at the zero crossing point:

$$\frac{I_0(\sigma/2)^2}{[(\nu - \nu_E)^2 + (\sigma/2)^2]} = \frac{I_0(\sigma/2)^2}{[(\nu - \nu_{E_r})^2 + (\sigma/2)^2]} . \tag{22}$$

When there is no change in peak width or intensity,

$$(\nu_z - \nu_E)^2 = (\nu_z - \nu_{E_r})^2 \tag{23}$$

which has the same solutions as for the Gaussian case above.

So, the "observed" peak shift of the zero crossing point will be half the actual peak shift in this special case. Notice that this relation is not true in Cases 6 and 7. Unfortunately, it is not necessarily possible to recognize from the difference spectra when conditions exist such that it is possible to benefit from this calculation. For example, if no adsorbate is gained or lost by an electrode surface with changing potential, and no major change in binding or adsorption takes place, so that peaks may shift in frequency but not in width, then exact determination of tuning rates and peak positions may be possible. Some difficulty may be encountered in determining when all of these conditions are met.

CONCLUSION

Except in special cases, there does not appear to be a simple solution to the problem of determining real peak shifts, intensities, exact peak frequencies, and peak widths from difference spectra collected using backgrounds containing absorption information from the molecule of interest. While we have shown that in some examples it is possible to extract at least qualitative information from the difference spectra, it is apparent that quantitative interpretations of difference spectra are generally impossible. In some cases, particularly where changes in peak widths are involved, even qualitative interpretations are not possible. Determinations of peak frequencies and shifts are particularly difficult to determine from difference spectra, while peak intensities show better agreement between the "real" and "observed" data, when the observed difference spectrum is not bipolar.

Much of the existing data from techniques such as SNIFTIRS, EMIRS, and other techniques dependent on difference spectra, come from simple molecules where single or non-overlapping spectral features may be observed. In this work, we have only looked at single spectral features, and have determined that in "real" difference spectra, we can only make some qualitative determinations from the data. For data with multiple overlapping peaks in the same spectral region, the problem with using difference spectra will be complicated much further, making a correct evaluation of the data more unlikely. For both single and multiple peaks, peak fitting may aid in reaching a reasonable interpretation of the data by identifying which peak characteristics may have changed. Peak fitting will not solve the problem of correct evaluation of difference spectra, but it may serve to limit the number of peak parameters that need to be considered. Through careful analysis of the system that is studied, and some peak fitting of the data, this work shows that some qualitative understanding of the data collected as difference spectra may be reached. In the best case for data where no information is available from the raw spectra, and where a constant peak width can be assumed from peak fitting, it will not be possible to determine the real peak position from the difference spectrum, any peak shift will occur in a real direction by an unknown amount, and the peak will have an intensity that is not very different from, yet not linearly related to, the true intensity of the peak of interest.

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TABLE 1

Gaussian Peak Parameters

	A	B	C	D	E	F
Case 1						
Peak Pos.	110	108	106	104	102	100
Peak Wid.	25.	25.	25.	25.	25.	25.
Peak Int.	10.	8.0	6.0	4.0	2.0	0
Case 2						
Peak Pos.	100	102	104	106	108	110
Peak Wid.	25.	25.	25.	25.	25.	25.
Peak Int.	10.	8.0	6.0	4.0	2.0	0
Case 3						
Peak Pos.	100	104	108	112	116	120
Peak Wid.	25.	25.	25.	25.	25.	25.
Peak Int.	10.	8.0	6.0	4.0	2.0	0
Case 4						
Peak Pos.	110	108	106	104	102	100
Peak Wid.	25.	25.	25.	25.	25.	25.
Peak Int.	25.	19.	15.	9.0	4.0	0
Case 5						
Peak Pos.	110	108	106	104	102	100
Peak Wid.	30.	27.	24.	21.	18.	15.
Peak Int.	25.	19.	15.	9.0	4.0	0
Case 6						
Peak Pos.	110	108	106	104	102	100
Peak Wid.	10.	10.	10.	10.	10.	10.
Peak Int.	15.	25.	20.	15.	10.	5
Case 7						
Peak Pos.	120	116	112	108	104	100
Peak Wid.	10.	10.	10.	10.	10.	10.
Peak Int.	25.	20.	15.	10.	5.0	0
Case 8						
Peak Pos.	110	108	106	104	102	100
Peak Wid.	10.	10.	10.	10.	10.	10.
Peak Int.	10.	10.	10.	10.	10.	10.

FIGURE CAPTIONS

Figure 1. I) The Gaussian peaks described by the parameters in Table 1, Case 1. II) The "observed" or difference spectra resulting when curve "A" is used as a reference.

Figure 2. Plots of "observed" wavenumbers vs. "real" wavenumbers for curves generated in Cases 1 through 5. The line for Case 1 follows the filled squares; Case 2 follows the filled triangles; Case 3 is shown by open triangles; Case 4 is graphed as open circles, and Case 5 as filled circles. The lines connecting the points are intended only as guides to the eye. Note that none of the lines falls in the region where "real" and "observed" data are the same.

Figure 3. I) The Gaussian peaks described by the parameters in Table 1, Case 2. II) The "observed" or difference spectra resulting when curve "A" is used as a reference.

Figure 4. Plots of "observed" intensities vs. "real" intensities for curves generated in Cases 1 through 5, plotted as a-e, respectively.

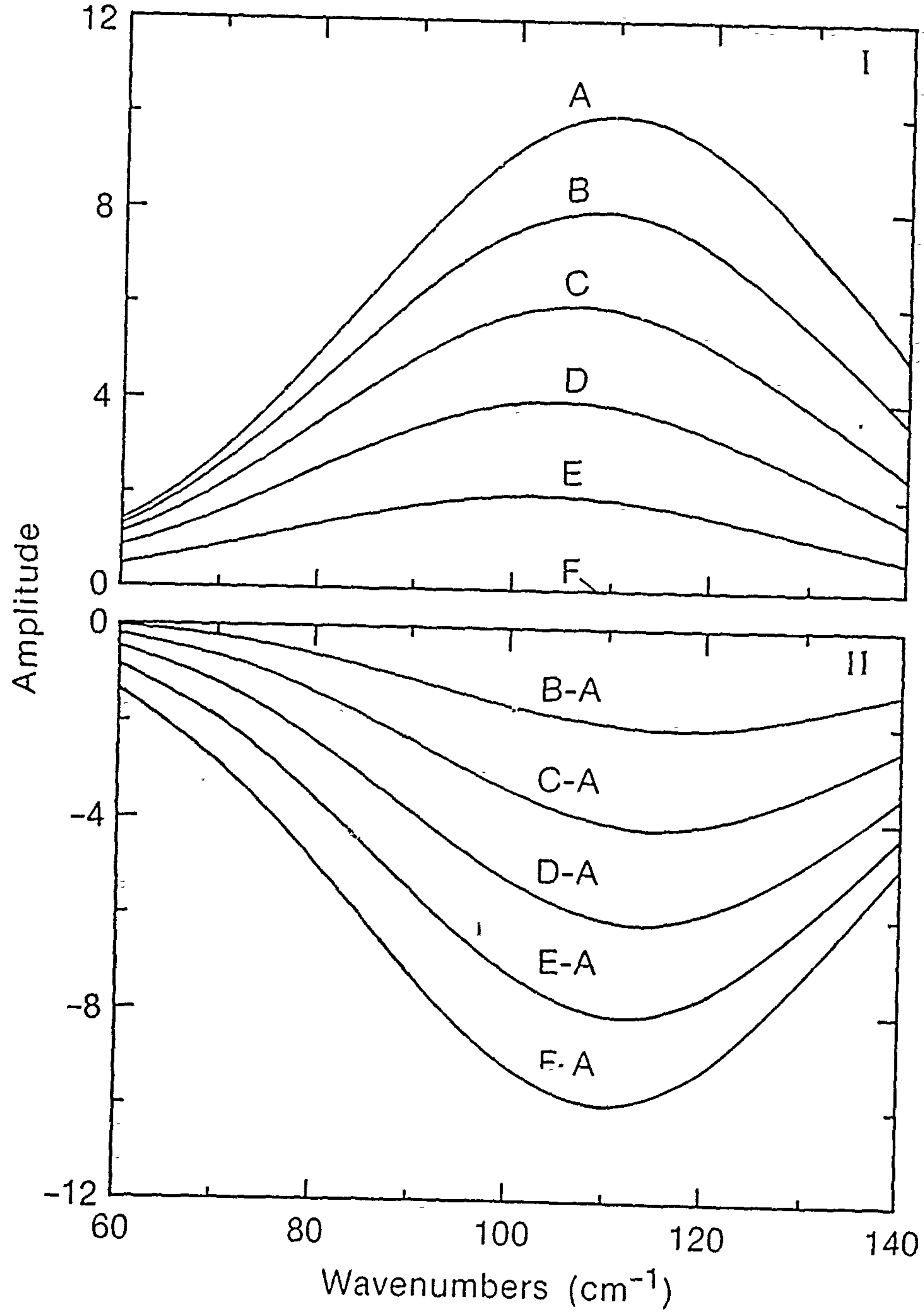
Figure 5. I) The Gaussian peaks described by the parameters in Table 1, Case 6. II) The "observed" or difference spectra resulting when curve "A" is used as a reference.

Figure 6. I) The Gaussian peaks described by the parameters in Table 1, Case 7. II) The "observed" or difference spectra resulting when curve "A" is used as a reference.

Figure 7. I) The Gaussian peaks described by the parameters in Table 1, Case 8. II) The "observed" or difference spectra resulting when curve "A" is used as a reference.

Figure 8. Plots of "observed" peak positions vs. "real" peak positions for a) Case 6, and b) Case 7. For these two examples, the filled squares denote the "observed" values for the negative peaks, the filled circles show the "observed" values for the positive peaks, and the filled triangles show the appearance of the line for the "real" peak positions plotted against themselves in each case.

Figure 9. Plots of "observed" intensities vs. "real" intensities for a) Case 6, and b) Case 7. For these two examples, the filled squares denote the "observed" values for the negative peaks, and the filled circles show the "observed" values for the positive peaks.



12
8
4
0
0
-4
-8
-12
I
II
A
B
C
D
E
F
B-A
C-A
D-A
E-A
F-A
Amplitude
60
80
100
120
140
Wavenumbers (cm^{-1})

Figure 1

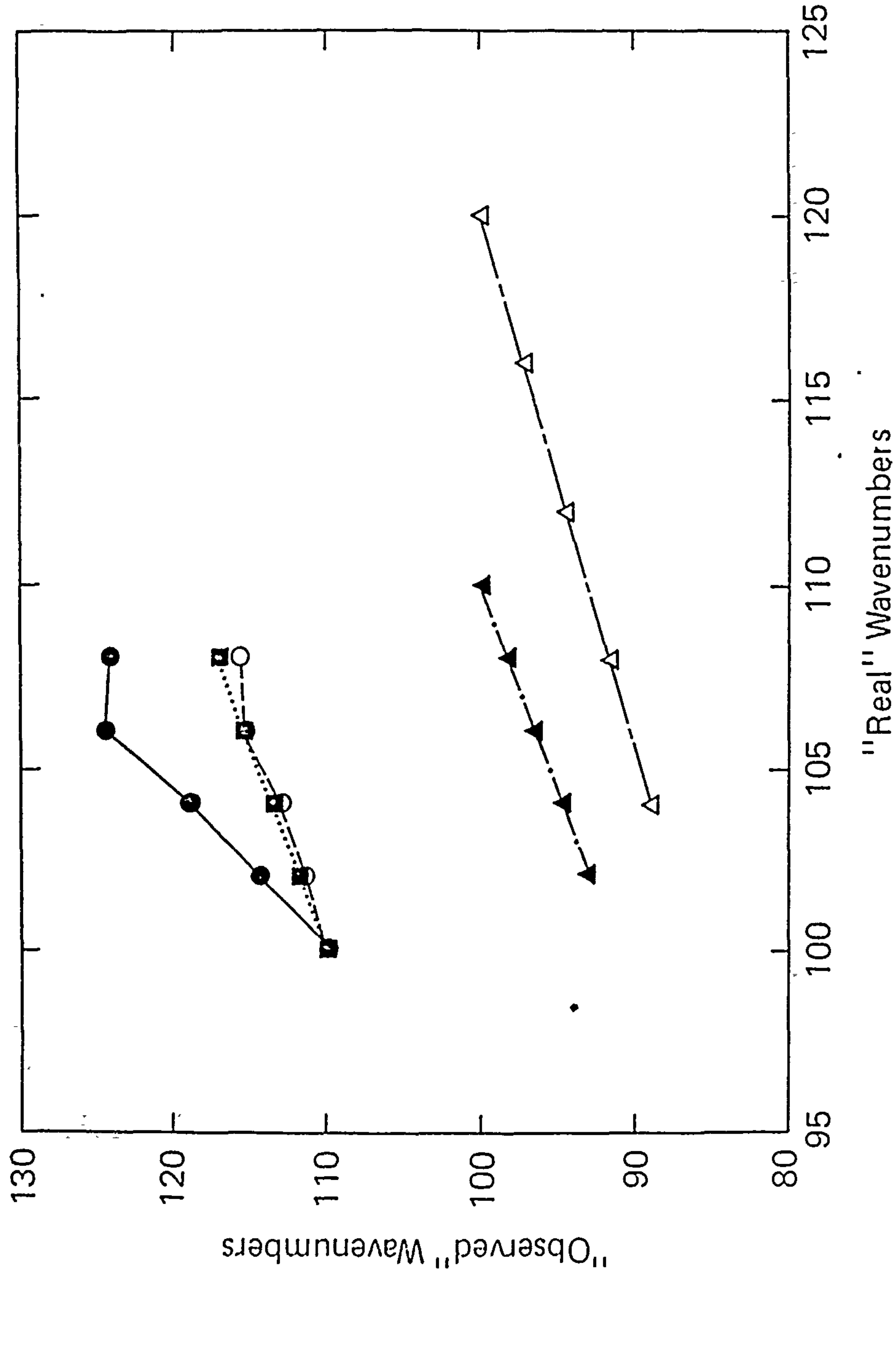

"Real" Wavenumbers
95
100
105
110
115
120
125
"Observed" Wavenumbers
80
90
100
110
120
130

Figure 2

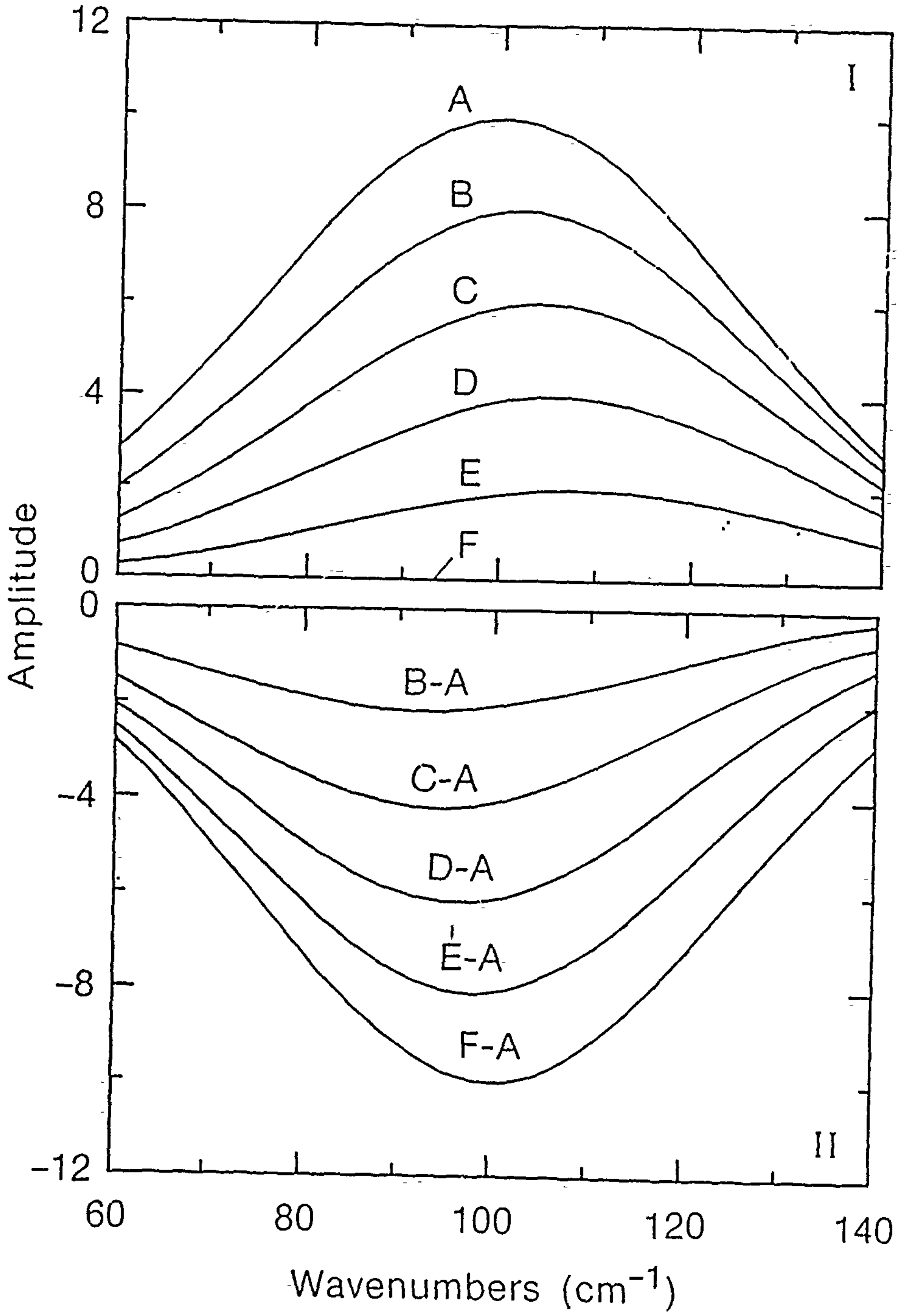

12
8
4
0
0
-4
-8
-12
I
II
A
B
C
D
E
F
B-A
C-A
D-A
E-A
F-A
Amplitude
60
80
100
120
140
Wavenumbers (cm^{-1})

Figure 3

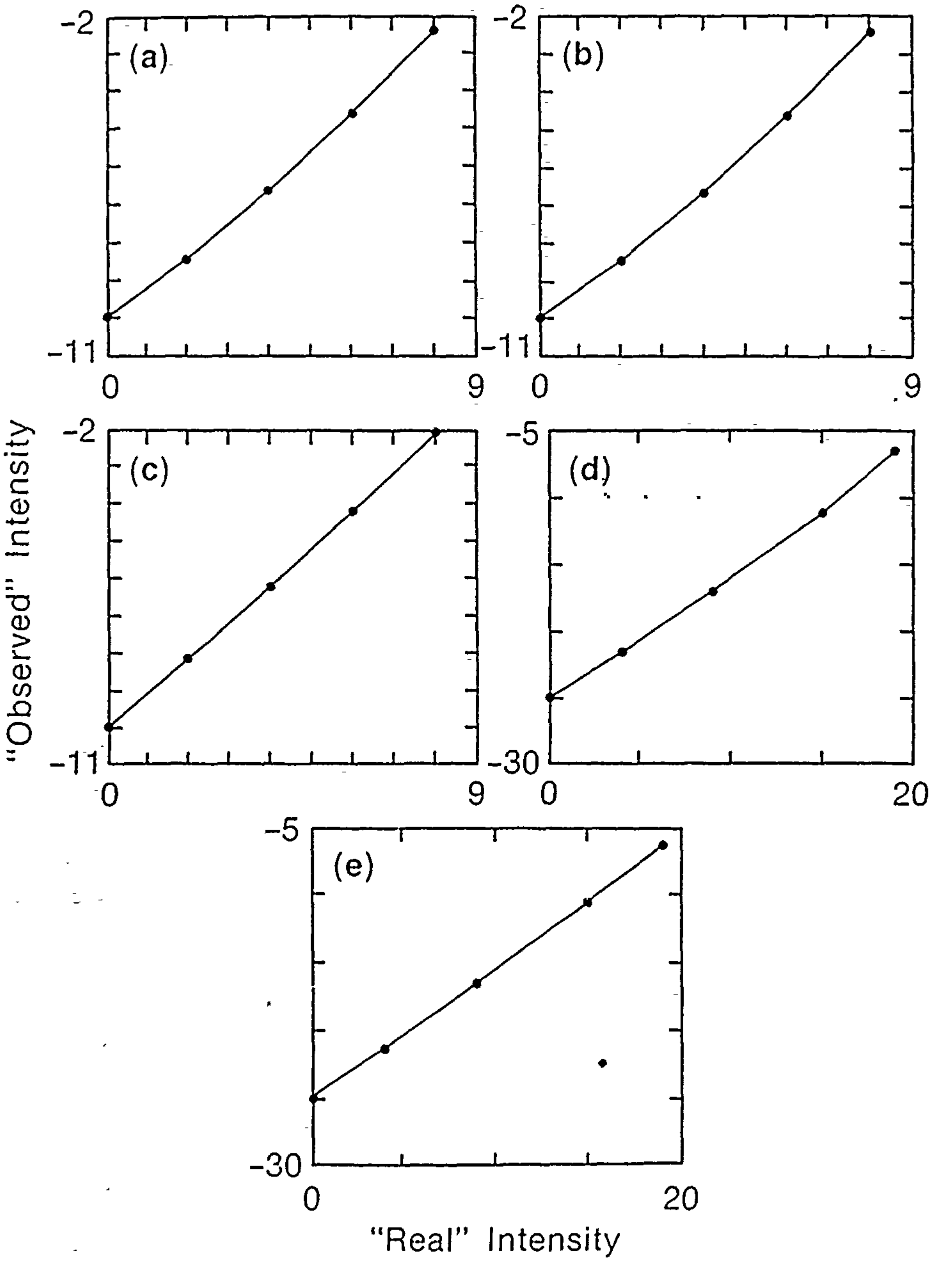
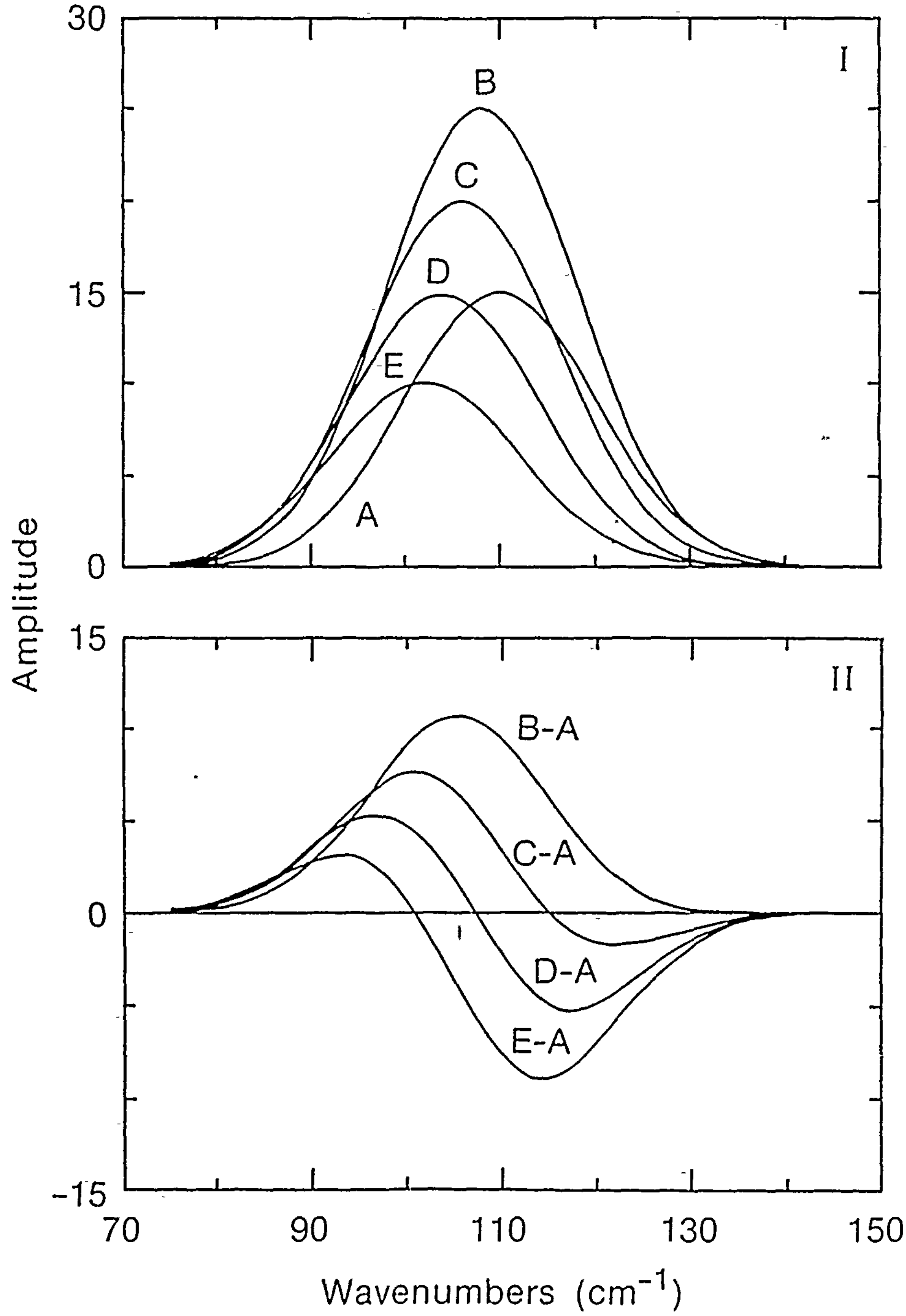


Figure 4



30
15
0
-15
I
II
B
C
D
E
A
B-A
C-A
D-A
E-A
Amplitude
70
90
110
130
150
Wavenumbers (cm-1)

Figure 5

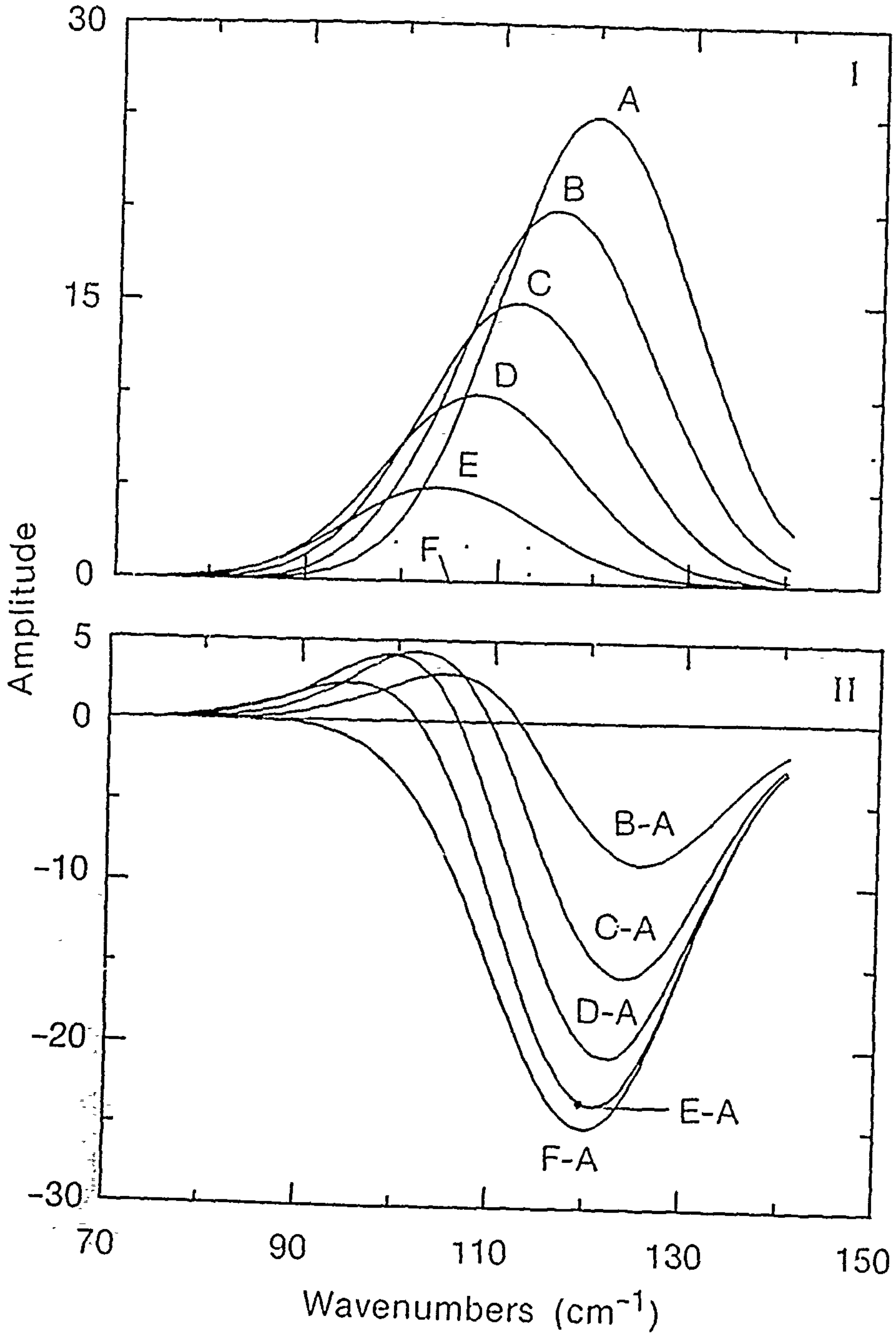
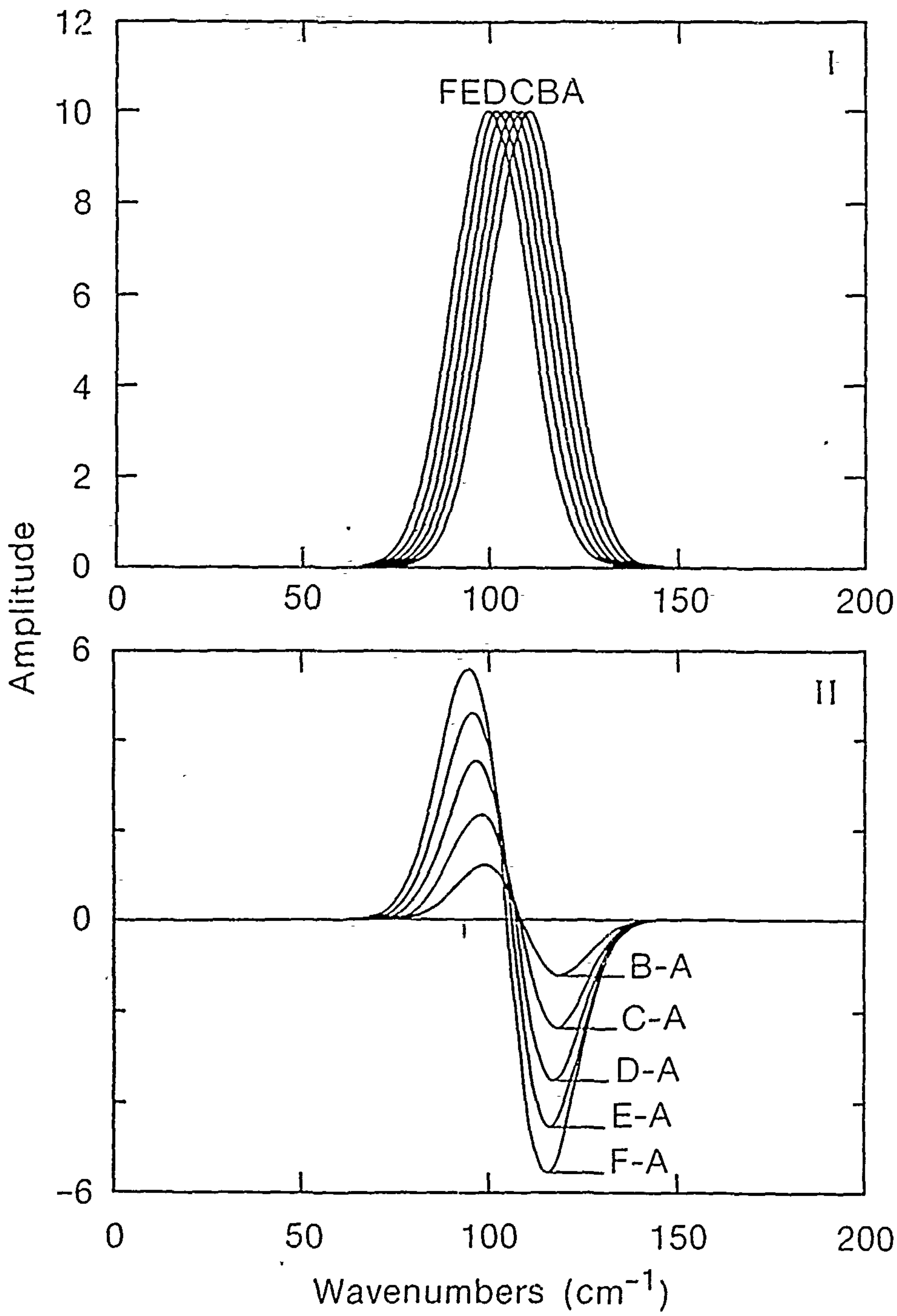
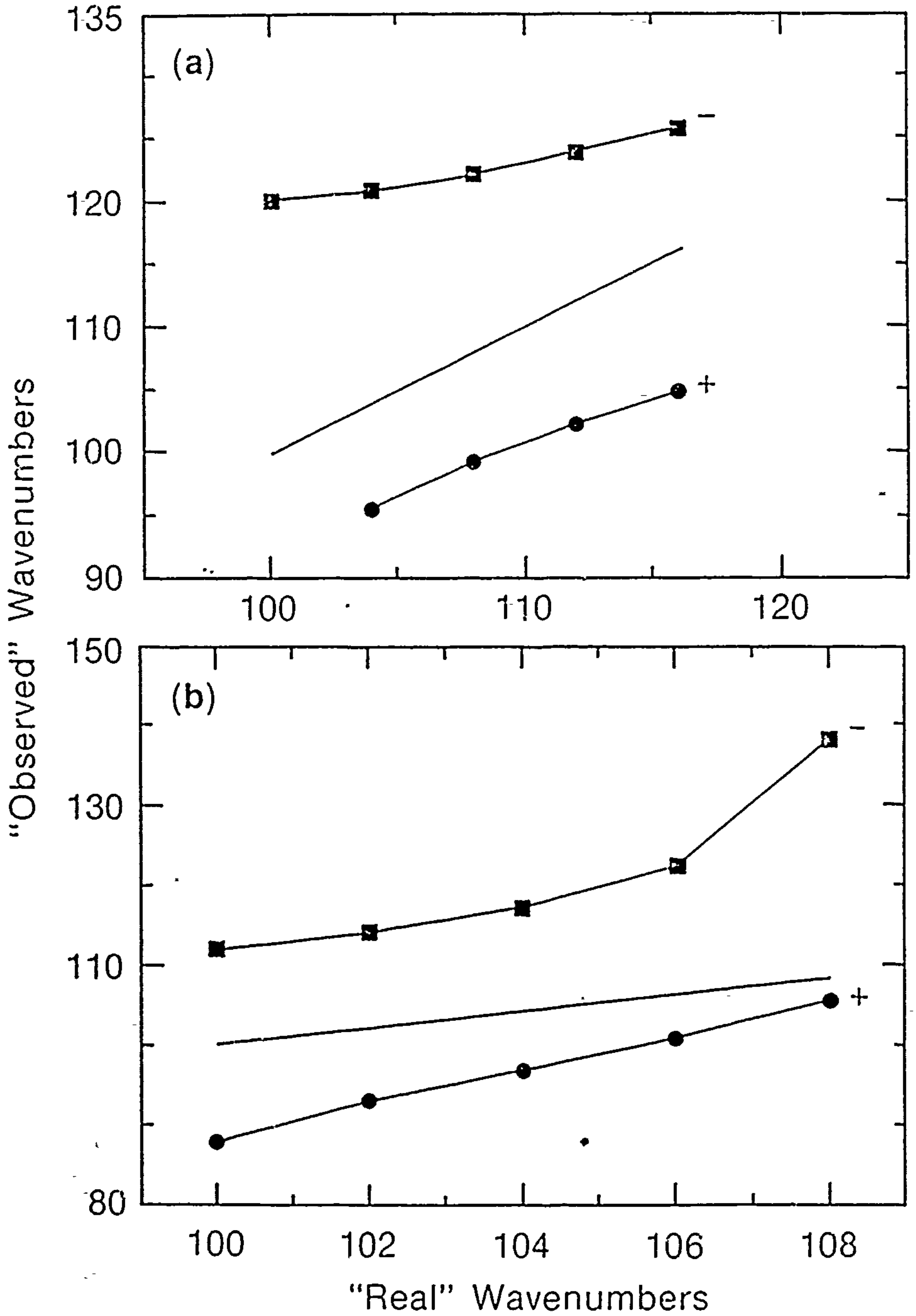

30
15
0
5
0
-10
-20
-30
70
90
110
130
150
Amplitude
Wavenumbers (cm^{-1})
I
A
B
C
D
E
F
II
B-A
C-A
D-A
E-A
F-A

Figure 6



12
10
8
6
4
2
0
I
FEDCBA
0
50
100
150
200
Amplitude
6
0
-6
II
B-A
C-A
D-A
E-A
F-A
0
50
100
150
200
Wavenumbers (cm^{-1})

Figure 7



135
120
110
100
90
(a)
−
+
100
110
120
150
130
110
80
(b)
−
+
100
102
104
106
108
"Observed" Wavenumbers
"Real" Wavenumbers

Figure 8

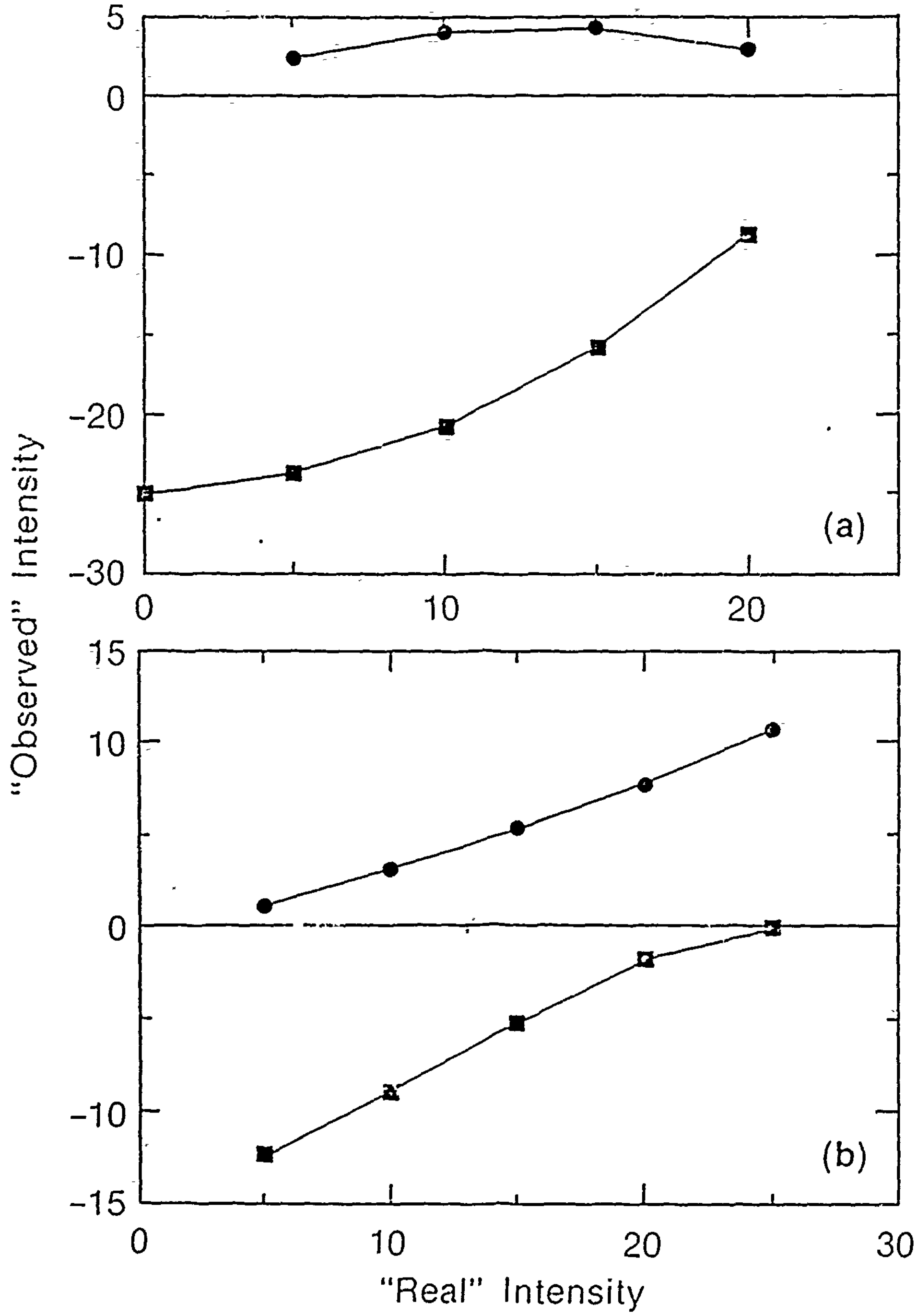

5
0
-10
-20
-30
(a)
0
10
20
15
10
0
-10
-15
(b)
0
10
20
30
"Observed" Intensity
"Real" Intensity

Figure 9